



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 5/08, C08K 5/54, 3/36, C09D 183/04	A1	(11) International Publication Number: WO 99/67336 (43) International Publication Date: 29 December 1999 (29.12.99)
(21) International Application Number: PCT/CA98/00673 (22) International Filing Date: 15 July 1998 (15.07.98) (30) Priority Data: 2,241,766 25 June 1998 (25.06.98) CA (71) Applicant (for all designated States except US): CSL SIL- ICONES INC. [CA/CA]; Suite 304, 365 Evans Avenue, Toronto, Ontario M8Z 1K2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): MISTRY, Balwantrai [CA/CA]; Unit 115, 49 Rhonda Road, Guelph, Ontario N1H 7A4 (CA). BARR, John, Richard [CA/CA]; 39 Lowrie Lane, Eden Mills, Ontario N0B 1P0 (CA). HUDA, Seraj, Ul [CA/CA]; 329 Lake Promenade, Toronto, Ontario M8W 1A6 (CA). (74) Agents: JOHNSON, Douglas, S. et al.; Dennison Associates, Suite 301, 133 Richmond West, Toronto, Ontario M5H 2L7 (CA).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: ONE-PART ORGANOPOLYSILOXANE RUBBER COMPOSITION FOR USE AS A CORROSION PROTECTION COATING ON METALS (57) Abstract <p>The present invention relates to a one-part room temperature vulcanizable organopolysiloxane rubber composition which crosslinks in the presence of moisture to form a coating for the corrosion protection of metals. The one-part organopolysiloxane rubber composition comprises the product which is obtained by mixing the following: a) about 20 to 50 weight percent of polydimethyl siloxane fluid of the formula: $\text{HO}[(\text{CH}_3)_2\text{SiO}]_n\text{H}$, in which n has an average value such that the viscosity is in the range from 1 to 100 Pa.S at 25 °C, preferably from 10 to 20 Pa.S at 25 °C; b) about 20 to 50 weight percent of a mixture of anorphorous and crystalline SiO_2 reinforcing fillers having a surface area of up to 200 m^2/g and a specific gravity of 2.2; c) about 2 to 6 weight percent of an oximino silane; d) about 0.25 to 2 weight percent of an organo functional silane; e) about 0.05 to 1 weight percent of an organotin salt; and f) about 10 to 40 weight percent of an organic solvent as a dispersion medium for the above composition.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	JP	Japan	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	KE	Kenya	NL	Netherlands	VN	Viet Nam
CG	Congo	KG	Kyrgyzstan	NO	Norway	YU	Yugoslavia
CH	Switzerland	KP	Democratic People's Republic of Korea	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KR	Republic of Korea	PL	Poland		
CM	Cameroon	KZ	Kazakhstan	PT	Portugal		
CN	China	LC	Saint Lucia	RO	Romania		
CU	Cuba	LI	Liechtenstein	RU	Russian Federation		
CZ	Czech Republic	LK	Sri Lanka	SD	Sudan		
DE	Germany	LR	Liberia	SE	Sweden		
DK	Denmark			SG	Singapore		
ER	Estonia						

TITLE: ONE-PART ORGANOPOLYSILOXANE RUBBER COMPOSITION
FOR USE AS A CORROSION PROTECTION COATING ON METALS

FIELD OF THE INVENTION

5 This invention relates to a one-part room temperature vulcanizable organopolysiloxane rubber composition which crosslinks in the presence of moisture to form a coating for the corrosion protection of metals.

10 BACKGROUND OF THE INVENTION

 Metal surfaces exposed to moisture such as rain or fog in combination with contaminated atmospheres as are found in industrial locations may be subject to extensive corrosion unless protected in some way from exposure to the
15 corrosive atmosphere. Other potentially corrosive environments include along sea coasts where salt spray is found and in areas where agricultural chemicals are widely distributed. In addition, metal surfaces directly exposed to water such as marine structures and vessels are also
20 subject to the potential for extensive corrosion. In the past, such metal surfaces have been most commonly protected by being painted with alkyd based paints. Such paints form a relatively rigid coating on the surface of the metal which can become brittle and when subjected to stress, can
25 flake or chip off, thereby exposing the underlying metal to the corrosive elements. In addition, such paints generally are susceptible to UV damage thereby further reducing their effective life.

 Two-part organopolysiloxane rubber compositions
30 for use as a corrosion protection coating on metals have been developed. For example, Lampe describes in U.S. Patent No. 4,341,842 a two-part room temperature vulcanizable composition for coating the underside of

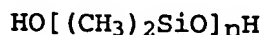
vehicles to protect the metal from rusting or being corroded by road salts or other similar compounds. However, such two-part compositions have a major disadvantage in that they require the use of complex dual mixing and spray nozzle apparatus or require pre-mixing and immediate use on site when used with conventional spray equipment. If conventional spray equipment is used, the amount of material pre-mixed must also be exact to prevent wastage as the composition has a finite pot life.

10

SUMMARY OF THE INVENTION

In one aspect the present invention provides for a one-part room temperature vulcanizing organopolysiloxane rubber composition for use as a corrosion protection coating on metals. The composition comprises the product which is obtained by mixing the following:

- a) about 20 to 50 weight percent of polydimethyl siloxane fluid of the formula



in which n has an average value such that the viscosity is in the range from 1 to 100 Pa.S at 25°C, preferably from 10 to 20 Pa.S at 25°C;

- b) about 20 to 50 weight percent of a mixture of anorphorous and crystalline SiO_2 reinforcing fillers having a surface area of up to 200 m^2/g and a specific gravity of 2.2;
- c) about 2 to 6 weight percent of an oximino silane;
- d) about 0.25 to 2 weight percent of an organo functional silane;
- e) about 0.05 to 1 weight percent of an organotin salt; and

- f) about 10 to 40 weight percent of an organic solvent as a dispersion medium for the above composition.

The present invention also provides for a method of protecting exposed surfaces particularly metal or concrete surfaces from the effects of a corrosive environment. The method comprises applying to the surface a thin layer of the above one-part organopolysiloxane rubber composition and allowing the layer of the one-part organopolysiloxane rubber composition to cure at room temperature to a silicone elastomer.

The present invention also provides for the metal or concrete surfaces coated with the silicone elastomer formed from the curing of the one-part organopolysiloxane rubber composition.

DETAILED DESCRIPTION OF THE INVENTION

The one-part organopolysiloxane rubber compositions of the present invention are ideally suited for corrosion protection of steel or concrete structures against salt spray and chemical environments including direct exposure to salt water, salt fog and other industrial pollutant. The compositions of the present invention can be used to coat metal surfaces of motor vehicles which may be exposed to high salt condition during the winter season. The compositions of the present invention are particularly useful on marine installations, electric transmission towers and bridges for corrosion protection of steel or concrete structures directly exposed to salt water and industrial pollution, especially sulfur based.

The one-part organopolysiloxane rubber compositions of the present invention for use as a corrosion protective coating on metals contain about 20 to

50 weight percent of polydimethylsiloxane fluid of the formula $\text{HO}[(\text{CH}_3)_2\text{SiO}]_n\text{H}$ in which n has an average value such that the viscosity is in the range from 1 to 100 Pa.S, preferably 10 to 80 Pa.S, most preferably 10 to 50 Pa.S at 25°C.

The composition also contains about 20 to 50 weight percent of a mixture of amorphous and crystalline SiO_2 reinforcing fillers having a surface area of up to 200 m^2/g and preferably a specific gravity of 2.2.

The composition also contains about 2 to 6 weight percent of an oximinosilane cross linking agent. Preferably the oximinosilane cross linking agent is of the formula $\text{RSi}(\text{ON}=\text{CR}'_2)_3$ in which R and R' each represent a monovalent hydrocarbon radical such as for example an alkyl radical such as methyl, ethyl, propyl, butyl, or an alkylene radical such as vinyl and allyl. The preferred R and R' are alkyl radicals, most preferably methyl and ethyl radicals.

The composition also contains about 0.25 to 2 weight percent of an organo functional silane. Preferably the organo functional silane has the formula



wherein R^2 and R^3 are C_{1-8} monovalent hydrocarbon radicals, b varies from 0 to 3, preferably 0, Z is a saturated, unsaturated or aromatic hydrocarbon which may be further functionalized by a member selected from the class consisting of amino, ether, epoxy, isocyanate, cyano, acryloxy and acyloxy and combinations thereof.

The C_{1-8} monovalent hydrocarbon radical of R^2 and R^3 includes an alkyl radical such as, for example, methyl,

ethyl, propyl, butyl, or an alkylene radical such as vinyl and allyl. Preferably R^2 and R^3 are alkyl radicals, more preferably methyl, ethyl or propyl radicals.

The saturated, unsaturated or aromatic hydrocarbon of Z includes alkyl, cycloalkyl, alkylene, and aryl groups. Among the alkyl groups are C_{1-8} straight or branched-chain alkyl such as, for example, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, etc., the cycloalkyl are C_{3-8} cycloalkyl such as, for example, cyclopropyl, cyclobutyl, cyclohexyl, etc., the alkylene groups are C_{1-8} alkylene such as, for example, vinyl, allyl, and the aryl groups include phenyl and naphthyl. The above groups may be further functionalized by including in the chain or ring structure, as the case may be, a group selected from the class consisting of amino, ether, epoxy, isocyanate, cyano, acryloxy, acyloxy and combinations. Preferably Z is an alkyl group, more preferably further functionalized by one or more amino group. The most preferred organo-functional silane is N-(2-aminoethyl-3-aminopropyl)trimethoxysilane.

The composition additionally contains about 0.05 to 1 weight percent of an organotin salt. Preferably the organotin salt is selected from the group dibutyltin diacetate, stannous octoate, dibutyltin dioctoate and dibutyltin dilaurate. Most preferably the organotin salt is dibutyltin dilaurate of the formula



The composition also contains about 10 to 40 weight percent of a hydrocarbon solvent to be used as a dispersion medium for the composition. The hydrocarbon solvent is preferably a petroleum based solvent such as naphtha or mineral spirits.

The composition may contain other optional ingredients such as pigments and other fillers in minor

amounts provided that the addition of the ingredients does not cause degradation of the corrosion resistance of the cured coating made from the composition. One commonly utilized optional ingredient is a pigment, preferably a grey pigment, most preferably present in amounts up to about 1 weight percent.

The organopolysiloxane composition of the present invention is prepared by mixing the ingredients together in the absence of moisture. The silane is moisture sensitive and will undergo cross-linking in the presence of moisture such that the mixture must be essentially absent of free moisture when the silane is added and maintained in a moisture free state until cure is desired.

A preferred method of mixing comprises mixing the polysiloxane polymer with the reinforcing fillers and other optional fillers and pigments. Thereafter, the oximinosilane and organo-functional silane are added and mixed under a nitrogen atmosphere. The solvent is added to the mixture under a nitrogen atmosphere and finally, the organotin salt is added to the mixture. The mixture is then dispensed in the sealed containers for storage prior to use.

The surface of the metal or concrete to be protected is coated with the composition by conventional methods such as dipping, brushing or spraying. Preferably, the metal or concrete to be protected is coated by spraying one or more applications of the composition of the present invention. The coating generally has an average thickness of 0.25 to 1.50 mm, single or more preferably, an average thickness of 0.5 to 1.0 mm, most preferably about 0.5 to 0.75 mm. After the coating is formed on the surface of the metal or concrete, the metal or concrete is exposed to normal atmosphere for cross-linking and cure of the coating.

The improved coating of the present invention is capable of protecting metal and concrete surfaces from corrosion in the presence of moisture such as rain or fog in combination with contaminated atmospheres, salt spray or fog or direct exposure to salt water.

The improved coating of the present invention is particularly useful for protecting metal surfaces which are directly exposed to salt water. Such surfaces include the hulls of ships and other vessels, oil drilling rigs, harbour and pier structures, etc. When the coating is used on the hulls of ships, further benefits such anti-fouling in addition to the corrosion protection are achieved. The coating does not allow marine animals, such as barnacles, to easily attach to the surface. Any such animals which attempt to attach to the surface are generally removed from the surface by high pressure washers. Additionally, clean up of the surface is generally accomplished by high pressure wash and/or hand or mechanical wiping and does not require the scraping operations commonly utilized during hull cleaning of ships, or other marine installations.

The following examples are included to illustrate preferred embodiments of the invention and to demonstrate the usefulness of the coating and are not intended to limit in any way the scope of protection for the invention.

25

EXAMPLE 1

To 36 parts of dimethyl polysiloxane fluid having a viscosity of 16.75 Pa.S at 25°C is added 35 parts of a mixture of anorphorous and crystalline silica fillers having a specific gravity of 2.2 and surface area of about 130m²/g. Then 2 parts of pigment is added and the composition is mixed in a mixer to a uniform consistency. Then 3 parts of methyl tris-(methyl ethyl ketoxime) silane and 1 part of N-(2-aminoethyl-3 aminopropyl)

trimethoxysilane are added and mixed under a nitrogen atmosphere. Then 22 parts of naphtha solvent is added to the mixture. Finally, 0.1 part of dibutyltin dilaurate is added to the dispersion and mixed until a uniform consistency is achieved.

Coupon samples prepared from stainless and carbon steel and aluminum sheet were coated with the composition prepared according to Example 1 by dipping into the mixture and exposing the samples to normal atmosphere for crosslinking. The coupon samples, having an average coating thickness of 0.3 mm, were exposed to salt-fog testing in an electrical (ozone producing) environment. After 2000 hours of continuous exposure, the coating showed no evidence of deterioration or separation from the virgin metal surfaces. Uncoated samples of both metals showed severe etching and corrosion.

Carbon steel sheet samples were coated with the composition according to Example 1 by dipping into the mixture and exposing the samples to normal atmosphere for crosslinking. The samples, having an average coating thickness of 0.3 mm, were exposed to accelerated heat aging at 260°C. After 7 days of continuous exposure, the coating showed no evidence of deterioration or separation from the virgin metal surface.

Carbon steel coupons coated with the composition of Example 1 to a thickness of 0.5 mm were immersed 30 days in an algae producing environment of ocean water at room temperature. Considerable deposits of algae were present which were easily removed by wiping with a damp cloth. The original surface of the coating showed no changes, scratches or deformations.

The improved flexibility of the coating and its resistance to cracking was confirmed utilizing carbon steel coupons coated with 0.3 mm thick coating. The samples were

bent 180° along a curve showed no cracks or separation from substrate.

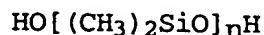
Compositions of the present invention are also useful for protecting other types of surfaces from
5 corrosive environments. For example, compositions of the present invention are particularly useful for protecting surfaces for spillage containment around tank farms and the like. The composition may be coated onto a heavy-duty fabric which is then utilized to line the interior of the
10 spillage catch basins around the tank farm. Samples of heavy-duty geo fabric were sprayed with the composition of the present invention to coat the fabric. Treated and untreated samples of fabric were exposed to caustic soda solution, diesel oil, furnace oil by placing samples of
15 these materials on the surface of the fabric for up to seven days. No deterioration of the treated fabric was observed and the deposits of the material were easily able to be cleaned up without any noticeable loss of weight of the material. In contrast, untreated fabric did not retain
20 the material on the surface and the caustic soda solution caused deterioration of the untreated fabric material within 24 hours.

While the invention has been described in
25 reference to specific embodiments it should be understood by those skilled in the art that various changes can be made and equivalents may be substituted without departing from the true spirit and scope of the invention. All such modifications are intended to be within the scope of the
30 claims appended hereto.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE AS FOLLOWS:

1. A one-part organopolysiloxane rubber composition
for use as a corrosion protection coating on metals
5 comprising the product which is obtained by mixing the
following:

- a) about 20 to 50 weight percent of polydimethyl
siloxane fluid of the formula



- 10 in which n has an average value such that the
viscosity is in the range from 1 to 100 Pa.S at
25°C, preferably from 10 to 20 Pa.S at 25°C;

- b) about 20 to 50 weight percent of a mixture of
anorphorous and crystalline SiO_2 reinforcing
15 fillers having a surface area of up to 200 m^2/g
and a specific gravity of 2.2;

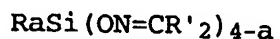
- c) about 2 to 6 weight percent of an oximinosilane;

- d) about 0.25 to 2 weight percent of an organo-
functional silane;

- 20 e). about 0.05 to 1 weight percent of an organotin
salt; and

- f) about 10 to 40 weight percent of an organic
solvent as a dispersion medium for the above
composition.

- 25 2. A composition according to claim 1 wherein the
oximinosilane is a compound of the formula



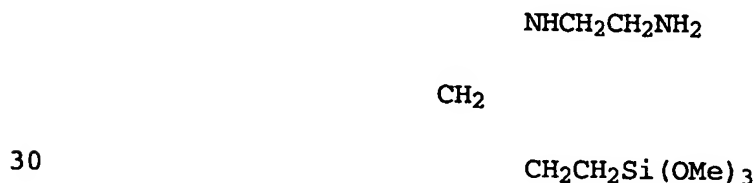
- 30 wherein R and R' represent a group of monovalent
hydrocarbon radicals and the integer a has a value 1,

3. A composition according to claim 2 wherein R and R' are independently selected from the group consisting of alkyl and alkylene.
4. A composition according to claim 2 wherein R and R' are each alkyl.
5. A composition according to claim 2 wherein R and R' are independently selected from the group consisting of methyl, ethyl, propyl, butyl, vinyl and allyl.
6. A composition according to claim 4 wherein R and R' are independently selected from the group consisting of methyl and ethyl.
7. A composition according to claim 1 wherein the organo-functional silane is a compound of the formula



wherein R² and R³ are C₁₋₈ monovalent hydrocarbon radicals, b varies from 0 to 3, preferably 0, Z is a saturated, unsaturated or aromatic hydrocarbon which may be further functionalized by a member selected from the class consisting of amino, ether, epoxy, isocyanate, cyano, acryloxy and acyloxy and combinations thereof;

8. A composition according to claim 1 wherein the organo functional silane is a compound of the formula



wherein Me is the methyl radical.

9. A composition according to claim 1 wherein the organotin salt is an organotin salt of a carboxylic acid selected from the group consisting of dibutyltin diacetate, stannous octoate and dibutyltin dioctoate.

10. A composition according to claim 9 wherein the organotin salt of a carboxylic acid is a compound of the formula

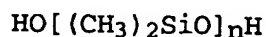


- 10 11. A composition according to claim 1 comprising:
- a) about 35 weight percent of a hydroxyl terminated dimethyl polysiloxane fluid having a viscosity of 10 Pa.S at 25°C;
 - b) about 35 weight percent of a mixture of anorphorous and crystalline SiO_2 fillers having a specific gravity of 2.2 and surface area of up to about $130\text{m}^2/\text{g}$;
 - c) about 4.3 weight percent of methyl tris-(methyl ethyl ketoxime)silane;
 - 20 d) about 2.2. weight percent of N-(2 aminoethyl-3 aminopropyl)trimethoxysilane;
 - e) about 0.8 weight percent of dibutyltin dilaurate;
 - f) about 22 weight percent of petroleum based solvent; and
 - 25 g) about 0.8 weight percent of a grey pigment.

12. A method of protecting a surface from the effects of a corrosive atmospheric environment comprising

(1) applying to the surface a thin layer of a one-part organopolysiloxane rubber composition comprising the product which is obtained by mixing the following:

- 5 a) about 20 to 50 weight percent of polydimethyl siloxane fluid of the formula



in which n has an average value such that the viscosity is in the range from 1 to 100 Pa.S at 25°C, preferably from 10 to 20 Pa.S at 25°C;

- 10 b) about 20 to 50 weight percent of a combination of anorphorous and crystalline SiO₂ reinforcing fillers having a surface area of up to 200 m²/g and specific gravity of 2.2;
- c) about 2 to 6 weight percent of an oximinosilane;
- 15 d) about 0.25 to 2 weight percent of an organo functional silane;
- e) about 0.05 to 1 weight percent of an organotin salt; and
- 20 f) about 10 to 40 weight percent of an organic solvent as a dispersion medium for the above composition.

and

(2) allowing the layer of the one-part organopolysiloxane rubber composition to cure at room temperature to a silicone elastomer.

25

13. A method according to claim 12 wherein the one part organopolysiloxane rubber composition comprises:

- 30 a) about 35 weight percent of a hydroxyl terminated dimethyl polysiloxane fluid having a viscosity of 10 Pa.S at 25°C;

- b) about 35 weight percent of a mixture of anorphorous and crystalline SiO_2 fillers having a specific gravity of 2.2 and surface area of up to about $130\text{m}^2/\text{g}$;
- 5 c) about 4.3 weight percent of methyl tris-(methyl ethyl ketoxime)silane;
- d) about 2.2. weight percent of N-(2 aminoethyl-3 aminopropyl)trimethoxysilane;
- e) about 0.8 weight percent of dibutyltindilaurate;
- 10 f) about 22 weight percent of petroleum based solvent; and
- g) about 0.8 weight percent of a grey pigment.

14. A method according to Claims 12 or 13 wherein the
- 15 surface to be protected is a metal or concrete surface exposed to a corrosive salt water environment.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 98/00673

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09D05/08 C08K5/54 C08K3/36 C09D183/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09D C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 340 120 A (RHONE-POULENC) 2 November 1989 see page 8, line 31 - page 9, line 7; claims 1,5	1-14
Y	EP 0 143 541 A (TORAY) 5 June 1985 see page 7, line 20 - line 24 see page 9, line 15 - line 25	1-14
Y	US 4 931 491 A (SAVIN) 5 June 1990 see column 4, line 22 - line 36	1-14
A	EP 0 735 101 A (DOW CORNING TORAY) 2 October 1996 see claim 1; example 1	1-14
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
Date of the actual completion of the international search 1 March 1999		Date of mailing of the international search report 17/03/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Lentz, J

INTERNATIONAL SEARCH REPORT

Int l Application No

PCT/CA 98/00673

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 734 479 A (INOUE ET AL) 29 March 1988 see column 7, line 60 - column 8, line 11; claim 1</p> <p>-----</p>	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 98/00673

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 340120 A	02-11-1989	FR 2629827 A AU 3251889 A CA 1316286 A JP 1306470 A US 4996112 A	13-10-1989 12-10-1989 13-04-1993 11-12-1989 26-02-1991
EP 143541 A	05-06-1985	JP 60096650 A AU 575868 B AU 3484284 A BR 8405243 A CA 1247775 A US 4535109 A	30-05-1985 11-08-1988 09-05-1985 27-08-1985 27-12-1988 13-08-1985
US 4931491 A	05-06-1990	NONE	
EP 735101 A	02-10-1996	JP 8269335 A CA 2172915 A US 5780543 A	15-10-1996 01-10-1996 14-07-1998
US 4734479 A	29-03-1988	JP 1669993 C JP 3033749 B JP 62223264 A	12-06-1992 20-05-1991 01-10-1987